

## OBSERVATION OF THE $^2P_{1/2} \leftarrow ^2P_{3/2}$ TRANSITION OF THE Br ATOM BY COLOR CENTER LASER SPECTROSCOPY\*

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The Br atom transition at  $3685 \text{ cm}^{-1}$  has been observed under high resolution by means of magnetic rotation spectroscopy using a color center laser. The isotope splitting between the center frequencies of the hyperfine patterns of  $^{79}\text{Br}$  and  $^{81}\text{Br}$  is  $13.6 \pm 0.2 \text{ MHz}$  with  $^{81}\text{Br}$  at higher frequency.

### 1. Introduction

The magnetic dipole allowed transition between the two lowest energy levels of the various halogen atoms is of considerable interest because it is possible to obtain lasing action between the two levels using a variety of schemes to prepare the inverted atom populations [1-4]. These transitions in Br and I have been measured in spontaneous emission using Fourier transform spectrometry with high accuracy [5]. This transition in Cl has been observed by means of laser magnetic resonance (LMR) [6] and diode laser spectroscopy [7].

In the present work, the Br atom transition at  $3685 \text{ cm}^{-1}$  was observed using a color center laser spectrometer and magnetic rotation spectroscopy with Doppler limited resolution. The isotope shift in the transition frequency between  $^{79}\text{Br}$  and  $^{81}\text{Br}$  is obtained from these measurements.

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### 2 Experimental

The overall experimental arrangement is shown in fig. 1. The color center laser source is a Burleigh model FCL-20 which has been modified for computer controlled operation by addition of a stepping motor drive for the grating. The intracavity etalon and folding mirror of the laser are driven by a Burleigh RC-42 ramp generator. These units in turn are controlled by a Digital Equipment Corp (DEC) LSI-11 minicom-

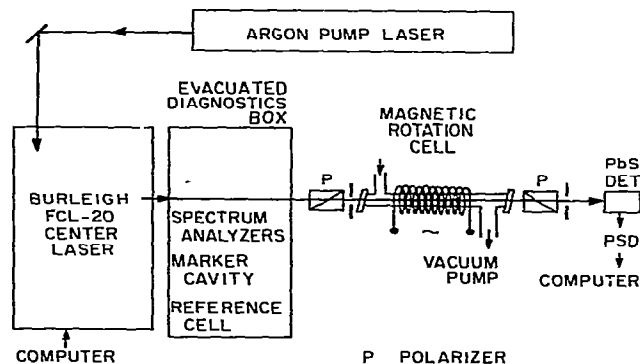


Fig 1 Experimental arrangement

puter through a Kinetic Systems 3912 controller and various CAMAC modules. A more complete description of the computer control system has been given previously [8].

The evacuated diagnostics box contains two spectrum analyzers, a 500 MHz marker cavity and gas cell which is used to provide a reference spectrum. The two spectrum analyzers provide continuous verification of single mode scan operation. The spectrum channel, the 500 MHz marker cavity transmission, and the reference spectrum are simultaneously acquired and stored in the computer thereby verifying the correctness of the frequency scale for the spectrum.

The Br atoms are prepared by the reaction of Br<sub>2</sub> with H atoms produced in a microwave discharge (2450 MHz) in water. The two reagents are mixed  $\approx 2$  cm upstream of the modulated region of the magnetic rotation cell and are flowed through the Zeeman modulation coil region  $\approx 20$  cm in length by the combined pumping of a liquid nitrogen cooled trap and a 5.5 l/s mechanical pump. The pyrex cell walls are coated with halocarbon wax (Halocarbon Corp.) which has been treated for several hours by slowly flowing a 3% mixture of fluorine in He at atmospheric pressure through the tube [9]. This treatment seems to replace the surface Cl atoms of the halocarbon wax with F atoms thereby creating an almost totally inert surface. With this surface, we have not been able to detect H atoms at the downstream end of the tube by the usual decrease in the pressure reading of the thermocouple gauge to below zero when the discharge is started. However, it is usually observed that the pressure reading decreases slightly on the opening of the Br<sub>2</sub> tap. We think that this decrease in pressure reading is due to the heating of the thermocouple sensing element by Br atom recombination.

In order to have sufficient sensitivity for the observation of the Br spectrum magnetic rotation was employed to reduce the source noise of the laser [10]. The modulation frequency of  $\approx 550$  Hz was chosen to coincide with a local minimum in the noise power spectrum of the laser output. With the MgF<sub>2</sub> Rochon polarizers employed which have an extinction ratio of  $\approx 10^{-3}$ , it appears that detector noise from the room temperature PbS detector is somewhat larger than laser noise at maximum extinction. Accordingly the polarizers were deliberately uncrossed until the noise showed a significant increase.

### 3. Observations

Fig. 2 shows a continuous single mode magnetic rotation scan over the Br atom transitions. The magnetic rotation signals of the  $1 \leftarrow 0$  and  $2 \leftarrow 1$  (R type) transitions have phases opposite of those of the other (P and Q type) transitions in agreement with theory. This scan exhibits all allowed hyperfine transitions of both <sup>79</sup>Br and <sup>81</sup>Br with every transition clearly resolved including the previously [5] unresolved  $2 \leftarrow 3$  transition. By using the known hyperfine splittings of the ground state [11], the splittings between the <sup>79</sup>Br and <sup>81</sup>Br features were measured. The measured splittings are listed in table 1. By using the accurately known hyperfine coupling constants of the ground [11] and excited [12] state, a value of the isotope shift in the fine structure spacing can be calculated from every entry. As can be seen the agreement between the values of the shift calculated from the various components is excellent. The values of the isotope shift obtained from the F 2-2, 1-2, and 1-1 components are probably somewhat more reliable than those obtained from the other three components. (The close agreement between the components thought to be

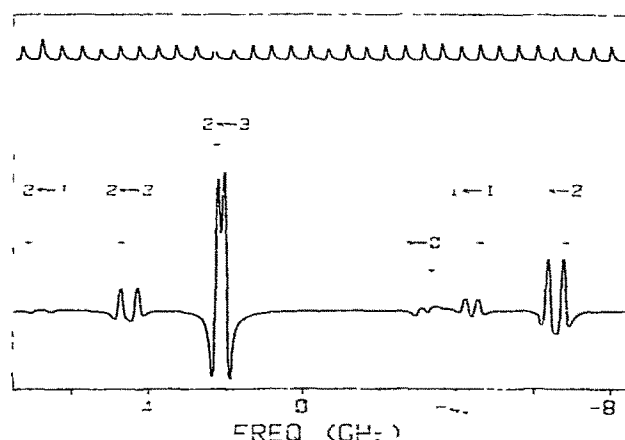


Fig. 2. Survey scan of the Br transition. The features marked with a + sign are <sup>81</sup>Br features while the unmarked features belong to <sup>79</sup>Br. This spectrum should be compared to the Fourier transform spectrum reported in ref. [5]. In magnetic rotation, the phases of the signals from  $1 \leftarrow 0$  and  $2 \leftarrow 1$  are expected to be opposite those of the other transitions as is observed. The marker cavity spacings are 491.5 MHz. The pressure was approximately 200 mTorr. The modulation field was 13 G (rms).

Table 1  
Isotope shift in the fine structure spacing of Br as measured from  $^{81}\text{Br}$  to  $^{79}\text{Br}$  splittings of each hyperfine component

$F'$	$F''$	$\Delta\nu(\text{obs})$ (MHz)	$\Delta\nu(\text{corr})^{\text{a)}}$ (MHz)	$\Delta\nu(1/2-3/2)$ (MHz)
2	3	157.8 <sup>b)</sup>	-140.7	17.0
2	2	424.5	-411.0	13.6
2	1	501.2 <sup>c)</sup>	-485.5	15.7
1	2	-407.0	420.3	13.3
1	1	-333.6	345.7	12.1
1	0	-322.4 <sup>c)</sup>	340.1	17.8

a) Calculated from the known hyperfine coupling constants of the ground [11] and excited [12] states

b) This splitting is affected by overlap of the two features

c) Poor signal-to-noise ratio and unexpected lineshape

somewhat more reliable is fortuitous. The scatter of all six results is more indicative of the precision.) The signal-to-noise ratio of the 2-1 and 1-0 features is significantly poorer and, more importantly, the line shapes obtained for these components are unaccountably distorted from that expected for a magnetic rotation signal. For the 2-3 component, the  $^{79}\text{Br}$  and  $^{81}\text{Br}$  signals are somewhat overlapped affecting the accuracy to which the splitting between them can be determined. Using the three hyperfine pairs which are expected to give the most accurate results, the final best value for the isotope shift in fine structure spacing is  $13.6_{-2}^{+5}$  MHz. This unsymmetrical error limit is chosen because none of the measurements suggest a value below 13 MHz while all of the less reliable points suggest values larger than 14 MHz.

#### 4 Discussion and conclusion

The isotopic shift in the transition frequency should be determined by the difference in the reduced mass of the electron and nucleus pair in the one-electron approximation\*. This predicted difference is 19 MHz with the  $^{81}\text{Br}$  transition frequency expected to be higher as compared to the experimental value of  $13.6_{-2}^{+5}$  MHz.

\* R. F. Code (1975) as reported by Dagenais et al. [6]

It is of some interest to consider the possibilities for increasing the resolution for these transitions beyond the Doppler limit. Because it is expected that the relaxation times for the internal states will be much longer than the time between velocity changing collisions, the whole of the Doppler profile is expected to saturate rather than a particular velocity group to which the laser is tuned. Thus it does not appear likely that saturation spectroscopy techniques will prove applicable to these transitions.

On the other hand, because the internal state relaxation times are expected to be long, it should be possible to saturate the whole velocity profile and thereby carry out both excited state and ground state microwave optical double resonance (MODR) experiments. Because the ground state splittings are known with such high accuracy [11], there seems little point in doing the ground state experiment. However, there is the possibility of achieving some improvement in accuracy to which the excited state hyperfine splittings [12] are known by MODR.

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